STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LII, 3, 2007

INVESTIGATION OF MICELLAR PROPERTIES OF ANIONIC SURFACTANTS WITH THE AID OF PVC-MEMBRANE DODECYL SULFATE ELECTRODE

SIMONA ANTOANELA GAVAN AND DAN FLORIN ANGHEL[*]

ABSTRACT. A polymer matrix electrode selective to anionic surfactants has been proposed. The active matter of the electrode was the dodecyltrimethylammonium dodecyl sulfate ion-pair. The matrix was made of high-molecular weight poly(vinyl chloride) (PVC) plastified with 2-nitrophenyl octyl ether. The electrode had Nernstian response with a slope of 57.3 ± 0.2 mV per decade over a range of dodecyl sulfate concentration from 3.5 x 10^{-6} to 6.0 x 10^{-3} M, and a detection limit of 2.2 x 10^{-6} M. The electrode was very selective towards inorganic interfering anions. Among the organic anions only those with surfactant properties did interfere. The working pH of the electrode was in the 3.0 - 13.0 range. The electrode was used to determine the critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS) in the absence and presence of water-soluble organic additives and of inorganic electrolytes.

INTRODUCTION

Due to the amphiphilic character, the surfactants aggregate at a threshold value of their concentration in solution. This value is called the critical micelle concentration (CMC), and is a fundamental characteristic that depends on surfactant composition and the additives present in the system. CMC is determined by many of methods, such as: surface tension [1], electrical conductivity [2], dye solubilization [3], UV-Vis spectrometry [4], fluorescence [5], scattering techniques [6,7], FTIR [8], viscosity [9], osmometry [10], nuclear magnetic resonance [11], electron spin resonance [12], isothermal titration calorimetry [13], etc. There are also reports on measuring the CMC by potentiometry with surfactant-selective electrode (SSE). The technique was developed by our group more than 30 years ago, and we originally emphasized that the discontinuity in the calibration curve corresponds to the CMC [14,15]. Nowadays, potentiometry with SSE is barely used for CMC determination [16,17], being mainly applied in surfactant analysis [18-22].

In this work, we describe the construction and characterization of a new dodecyl sulfate selective electrode. The electrode was used to determine the CMC of sodium dodecyl sulfate (SDS) in aqueous solution in the absence and presence of inorganic electrolytes and organic additives.

---

[*] Romanian Academy, "Ilie Murgulescu" Institute of Physical Chemistry, Department of Colloids, Spl. Independentei 202, 060021 Bucharest, Romania

EXPERIMENTAL PART

Materials

All the chemicals were analytical grade reagents and were used as received. The surfactants were purchased from Serva (SDS), and Fluka (dodecyltrimethylammonium bromide, DTAB). The high molecular mass poly(vinyl chloride) and the plasticizer 2-nitrophenyl octyl ether (NPOE) were also Fluka products. Tetrahydrofuran was purchased from Merck. The water used to prepare the solutions was ultrapure water with a resistivity of 18.2 MΩ.cm at 25^{o} C.

Apparatus

The potential measurements were made with a digital ORION pH-meter, model 420A (ATI ORION Boston, U.S.A.). The reference electrode was the Ag/AgCl model 900200 (ATI ORION, Boston, U.S.A.). The pH measurements were made with a glass electrode model P-05992-40, (COLE PARMER INSTRUMENT COMPANY, Vernon Hills, U.S.A.). The ultrapure water was prepared with the aid of Simplicity UV apparatus (MILLIPORE SAS, Molsheim, France).

Preparation of the ion-pair complex

The dodecyltrimethylammonium dodecyl sulfate ion-pair was obtained by drop-wise addition of 0.005 M SDS aqueous solution into 0.005 M DTAB aqueous solution. The ion-pair precipitate was extracted in chloroform. The organic layer was separated and dried over anhydrous sodium sulfate. The inorganic salt was removed by filtration, and the ion-pair was recovered by gentle evaporation of the organic solvent.

Membrane preparation

The ion-pair complex (10 mg) was mixed with 0.35 mL of 2-nitrophenyl octyl ether, 0.19 g of poly(vinyl chloride) powder and 5 mL of tetrahydrofuran. The solution was poured into a glass ring resting on a clean glass plate. A wad of filter papers, weighted down with a heavy weight, was placed on top of the ring and the whole assembly left at room temperature to evaporate the solvent.

Construction of electrode

Disks of 10 mm in diameter were cut from the master membrane with a cork borer and glued to the flat end of the hollow PVC support tube with an adhesive of PVC in tetrahydrofuran. The tube was filled with a 1:1 mixture of aqueous 10^{-3} M SDS and 10^{-3} M sodium chloride solutions and inserted into the inner reference saturated calomel electrode.

The electro-chemical cell contains the measuring solution, the surfactant selective electrode and the reference Ag/AgCl electrode.

RESULTS AND DISCUSSION

Electrode characterization

The procedure of electrode characterization consists of recording the calibration curve, response time, effect of pH and selectivity. All are important parameters in designing the electrode and estimating its performance.

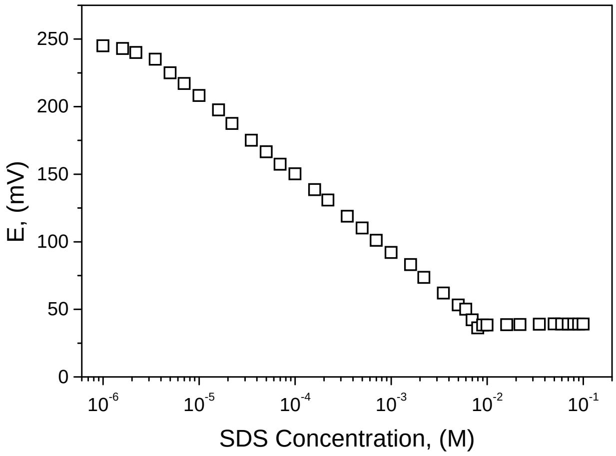

Figure 1. The calibration curve of DS-selective electrode at 25^{o} C.

Figure 1 shows the results obtained at electrode calibration in SDS solutions at 25^{o} C. The curve is linear in-between 3.5 x 10^{-6} and 6.0 x 10^{-3} M SDS. At 8.0 x 10^{-3} M, the calibration curve has a breaking point assigned by us to the formation of surfactant micelles into solution. The figure is within the range of values (7.1 – 8.3) x 10^{-3} M reported in literature [23-25]. After CMC, the recorded potential is practically constant. This is in accord with the theory of surfactant micellization which predicts that all the surfactant introduced into the system above CMC forms micelles, and the concentration of free surfactant is constant.

The linear fit of potential values within the linear range of electrode response resulted in a slope of 57.3 ± 0.22 mV/decade of SDS concentration and a regression coefficient of 0,99986. Both the slope and the regression coefficient prove the good performance and quality of the electrode and allowed us to consider it for further steps of characterization.

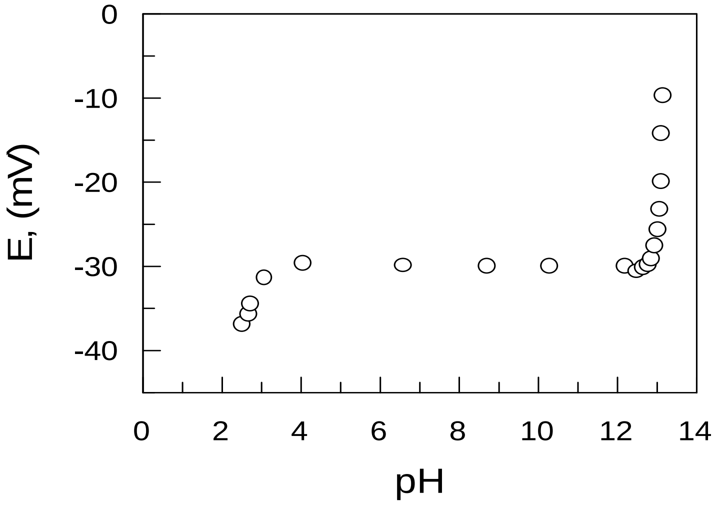

Figure 2. The influence of pH upon the SD-selective electrode.

Time of response and lifetime

The response time is the period elapsed between the moment when the DS-selective electrode and the reference electrode are brought into contact with a sample solution (or at which the activity of the ion of interest in solution is changed) and the first instant at which the slope of the cell potential vs. time plot (ΔE/Δt) becomes equal to a limiting value selected to be of 0.6 mV/min [25]. The response of electrode was very fast. Within the linear range of the calibration curve, the elapse time was of maximum 5 seconds within the range of linear response. Within the same range, a set of 10 calibrations gave reproducible potentials with an error of ± 2.0 mV/day. At very low surfactant levels, the lapse time increased to 2 - 5 minutes.

The lifetime of the electrode was of four months. After that it had erratic response, the membrane lost elasticity and became opaque. We suspect responsible for this behavior the loss of plasticizer by diffusion.

Effect of pH

The influence of hydrogen ions on the electrode was determined at a constant surfactant concentration of 1.0 x 10^{-3} M SDS. The pH was changed by means of minute amounts of concentrated hydrochloric acid and sodium hydroxide solutions. The modification of pH was monitored with the glass electrode. After every pH change, it was waited until the surfactant selective electrode stabilized its reading. Figure 3 illustrates the results obtained. One may observe that the electrode potential is not affected by pH in the 3.0 -13.0 range. This large pH working range will allow to use the electrode both in surfactant and soap titrations.

Selectivity of electrode

Electrode selectivity is defined by means of the potentiometric selectivity coefficients and it is an important parameter in designing a suitable electrode. The selectivity coefficient, $K_{i,j}^{pot}$, defines the ability of an ion-selective electrode to distinguish a particular ion, i, from others, j [26]. Usually $K_{i,j}^{pot}$, has values in-between 10^{-4} and 10^{4}, but it may fall outside this range. The smaller the value of $K_{i,j}^{pot}$, the greater the preference of the electrode for the principal ion.

In our case, the selectivity coefficient, $K_{DS,j}^{pot}$, was evaluated by measuring the electromotive force (EMF) of ion-selective electrode in separate solutions of principal ion, DS, and interfering ion, j. For a solution containing only the primary ion, the electrode potential is given by equation (1):

$$E_1 = E^{01} + (RT/F)\ln a_{DS} \qquad (1)$$

In a solution of only the interfering ion the electrode potential is:

$$E_2 = E^{02} + (RT/F)\ln a_{DS} + (RT/F)\ln K_{DS,j}^{pot} \qquad (2)$$

If $a_{DS} = a_j$, by converting to decimal logarithm, one obtains:

$$\lg K_{DS,j}^{pot} = (E_2 - E_1)\ F/(2.303\ RT) \qquad (3)$$

Relation (3) permits to determine the potentiometric selectivity coefficients from the recorded values of the E_1 and E_2. The values obtained by us for $K_{DS,j}^{pot}$ are given in Table 1. The selectivity coefficient values show that the electrode has excellent selectivity for the DS ion over inorganic anions. The same holds true for organic anions like formate, acetate and propionate, and for short-chain alkyl sulfates and sulfonates. For sulfates and sulfonates, the interference increases with the length of the alkyl chain. However, this apparent disadvantage offers the possibility of using the electrode as end-point detector in potentiometric titration of anionic surfactants, irrespective of their alkyl chain length.

Table 1.

Selectivity coefficients of dodecyl sulfate electrode

Interferent anion, j	a_j, (M)	$K_{DS,j}^{pot}$
Cl^-	10^{-3}	4.07×10^{-4}
Br^-	10^{-3}	5.25×10^{-4}
I^-	10^{-3}	5.74×10^{-4}
SO_4^{2-}	10^{-3}	2.63×10^{-7}
$HCOO^-$	10^{-3}	6.33×10^{-5}
CH_3COO^-	10^{-3}	9.12×10^{-4}
$C_2H_5COO^-$	10^{-3}	1.27×10^{-3}
$C_5H_{11}SO_4^-$	10^{-3}	1.40×10^{-3}
$C_8H_{17}SO_4^-$	10^{-3}	0.01
$C_{10}H_{21}SO_4^-$	10^{-3}	0.33
$C_{12}H_{25}SO_4^-$	10^{-3}	1.00
$C_{14}H_{29}SO_4^-$	10^{-3}	65.1
$C_{16}H_{33}SO_4^-$	5×10^{-4}	113.2
$C_5H_{11}SO_3^-$	10^{-3}	0.94×10^{-4}
$C_8H_{17}SO_4^-$	10^{-3}	0.011
$C_{12}H_{25}SO_3^-$	10^{-3}	0.96
$C_{14}H_{29}SO_3^-$	10^{-3}	58.3
$C_{12}H_{25}C_6H_4SO_3^-$	10^{-3}	105.6

Determination of CMC

Micelles that form in dilute aqueous solutions are affected by the additives present in the system. Previous works have demonstrated that electrolytes usually decrease the CMC [27-29], whereas hydrophobic solubilizates entail the increase of spherical micelles to ellipsoids and rods [30,31].

The data in Table 2 show that CMC decreases by increasing the electrolyte concentration. The result can be explained taking into account the attraction and adsorption of counterions at the ionic micelle surface. The phenomenon stabilizes the micelle surface in an extent that depends on the micelle charge density. At the same time, there is a gradual change in the counterion-micelle interaction as the electrolyte concentration increases. The higher is the electrolyte concentration, the higher is the adsorption of counterions and the lower is the CMC.

Table 2.

Effect of electrolytes on the CMC of SDS at 298 K

Electrolyte	Concentration (M)	CMC Electrode (M)	CMC Literature (M)	Reference
-	-	8.0×10^{-3}	$(7.1\text{-}8.3) \times 10^{-3}$	24,25
NaCl	10^{-3}	7.0×10^{-3}	6.90×10^{-3}	23
	10^{-2}	5.6×10^{-3}	5.62×10^{-3}	23
	10^{-1}	1.5×10^{-3}	1.49×10^{-3}	23
NaBr	10^{-1}	1.4×10^{-3}	1.42×10^{-3}	23
NaF	10^{-1}	1.6×10^{-3}	1.45×10^{-3}	23
NaI	10^{-1}	1.3×10^{-3}	1.38×10^{-3}	23

Table 3.

Effect of organic additives on the CMC of SDS at 298 K

Organic Additive	Concentration (wt. %)	CMC Electrode (M)	CMC Literature (M)	Reference
-	-	8.0×10^{-3}	$(7.1\text{-}8.3) \times 10^{-3}$	24, 25
Methanol	25.0	9.0×10^{-3}	-	This work-
Ethanol	5.0	5.5×10^{-3}	1.07×10^{-2}	23
	10.0	6.5×10^{-3}	5.96×10^{-3}	23
	25.0	1.1×10^{-2}	1.07×10^{-2}	23
	30.0	2.0×10^{-2}	1.90×10^{-2}	16
	40.0	4.0×10^{-2}	4.20×10^{-2}	16
1-Propanol	5.0	4.0×10^{-3}	4.40×10^{-3}	16
	10.0	5.0×10^{-3}	5.20×10^{-3}	16
	20.0	1.3×10^{-2}	1.35×10^{-2}	16
2-Propanol	5.0	4.0×10^{-3}	4.3×10^{-3}	23
Dioxane	5.0	8.0×10^{-3}	7.7×10^{-3}	23
	10.0	1.0×10^{-2}	9.0×10^{-3}	23
	20.0	2.0×10^{-2}	2.12×10^{-2}	23

The aggregation of SDS in ethanol- and *n*-propanol-water mixtures was formerly investigated with the aid of a dodecyl sulfate selective electrode [16]. A decrease of CMC at low and moderate alcohol content and an increase at high additive levels was observed, the effect being more evident for *n*-propanol. Table 3 presents the data obtained by us for short alkyl chain alcohols and dioxane. The trend is similar to that previously observed [16]. The results might be explained by the ability of alcohols to adsorb near the head group region of surfactant micelle, with the alcohol groups in between the ionic groups. The process reduces the electrical repulsion and lowers the CMC. High concentrations of short-chain alcohols influence the solvent characteristics of water, improve the surfactant solubility and therefore increase the CMC.

CONCLUSIONS AND PERSPECTIVES

A new, easy to construct, and reliable dodecyl sulfate-selective electrode is described. The electrode has Nernstian slope, instantaneous response, good stability in time and a working pH range in-between 3.0 and 13.0. The electrode is characterized by good selectivity towards inorganic anions. Among the organic interferents tested, only those having surface-active properties do interfere, and the interference rises with the hydrophobic character of the surfactant. The electrode performs well in measuring the critical micelle concentration of SDS both in the absence and presence of inorganic electrolytes and organic water-miscible additives.

Work is in progress now in our laboratory to improve the electrode lifetime by using polymeric plasticizers that diffuse slowly, or not at all, from membrane. We also undertake a study on systems of water-soluble polymers and anionic surfactants. It aims to construct the binding isotherms, to obtain the binding parameters and to determine the effect of additives on them.

ACKNOWLEDGMENT

We thank CNCSIS for financial support (Grant No. 201/2006).

REFERENCES

1. B. Z. Putlitz, H. P. Hentze, K. Landfester, M. Antonietti, *Langmuir* **2000,** *16,* 3214-3220.
2. N. Jiang, P. Li, Y. Wang, J. Wang, H. Yan, R. K. Thomas, *J. Colloid. Interface. Sci*., **2005**, *286*, 755-760.
3. N. Zhang, S. R. Guo, H. Q. Li, L. Liu, Z. H. Li, J. R. Gu, *Macromol. Chem. Phys*., **2006**, *207*, 1359-1367.
4. J. Zhang, B. Dong, L. Q. Zheng, G. Z. Li, *Colloid. Surf. A*, **2006**, *290*, 157-163.
5. C. Q. Zhu, Y. Q. Wu, H. Zheng, J. L. Chen, S. J. Zhuo, Y. X. Li, *Anal. Bioanal. Chem.*, **2004**, *379*, 730–734.
6. P. C. Griffiths, M. L. Whatton, R. J. Abbott, W. Kwan, A. R. Pitt, A. M. Howe, S. M. King, R. K. Heenan, *Journal Colloid Interface Sci.*, **1999**, *215*, 114–123.
7. L. T. Okano, F. H. Quina, O. A. El Seoud, *Langmuir* **2000,** *16,* 3119-3123.
8. L. Carolei, I. G. R. Gutz, *Talanta*, **2005**, *66*, 118-124.
9. S. Shirai, S. Yoshimura, Y. Einaga, *Polym. J.*, **2006**, *38*, 37-43.
10. V. B. Wagle, V. G. Gaikar, *J. Chem. Engn. Data*, **2006**, *51*, 886-891.
11. P. C. Griffiths, E. Pettersson, P. Stilbs, A. Y. F. Cheung, A. M. Howe, A. R. Pitt, *Langmuir* **2001,** *17,* 7178-7181.
12. M. A. Bahri, M. Höbeke, A. Grammenos, L. Delanaye, N. Vandewalle, A. Seret, *Colloid. Surf. A*, **2006**, *290*, 206-212.
13. M. Prasad, I.Chakraborty, A.R: Rakshit, S. P. Moulik, *J. Phys. Chem. B*, **2006**, *110*, 9815-9821.
14. D. F. Anghel, N. Ciocan, *Colloid Polym. Sci*., **1976**, *254*, 114-115.
15. N. Ciocan, D. F. Anghel, *Tenside Deterg*., **1976**, *13*, 188-192.
16. A. A. Rafati, H. Gharibi, M. Rezaie-Sameti, *J. Mol. Liq*., **2004**, *111*, 109-116.
17. K. Nesmerak, I Nemcova, *Anal. Lett*., **2006**, *39*, 1023-1040.

18. G. A. E. Mostafa, *J. Pharm. Biomed. Anal*., **2006**, *41*, 1110-1115.
19. T. Masadome, K. Yada, S. I. Wakida, *Anal. Sci*., **2006**, *22*, 1065-1069.
20. M. A. Plesha, B. J. van Wie, J. M. Mullin, D. A. Kidwell, *Anal. Chim. Acta*, **2006**, *570*, 186-194.
21. S. Martinez Barrachina, M. del Valle, *Microchem. J*., **2006**, *83*, 48-54.
22. M. Sak-Bosnar, D. Madunic-Cacic, R. Matesic-Puac, Z. Grabaric, *Anal. Chim. Acta*, **2007**, *581*, 355–363.
23. P. Mukerjee, K. J. Mysels, “Critical Micelle Concentrations of Aqueous Surfactant Systems”, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U. S.), Washington, D.C., **1971**.
24. M. N. van Oss, J. R. Haak, L. A. M. Rupert, “Physico-Chemical Properties of Selected Anionic, Cationic and Nonionic Surfactants”, Elsevier, Amsterdam, **1993**.
25. B. Antalek, J. Kowalczyk, C. Krishnan, *Langmuir*, **2004,** *20,* 11818-11820.
26. R. P. Buck, E. Lindner, *Pure Appl. Chem.,* **1994**, *66*, 2527-2536.
27. M. Pisarcik, F. Devinsky, I. Lacko, *Colloids Surf. A*, **2000**, *172*, 139–144.
28. S. S. Shah, N. U. Jamroz, Q. M. Sharif, *Colloids Surf. A*, **2001,** *178*, 199–206.
29. S. Miyagishi, N. Takeuchi, T. Asakawa, M. Inoh, *Colloids Surf. A*, **2002,** *197*, 125–132.
30. I. Johnson, G. Olofsson, M. Landgren, B. Jonsson, *J. Chem. Soc., Faraday Trans. 1*, **1989**, *85*, 4211–4226.
31. R. De Lisi, S. Milioto, R. E. Verral, *J. Solut. Chem*., **1990**, *19*, 639–664.